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Electrochemical Parameterization of Rhenium Redox Couples

By

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"Electrochemical Parameterization of Rhenium Redox Couples"

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Abstract

The observed rhenium potentials for $Re^{IV/III}$, $Re^{III/II}$ and $Re^{II/I}$ reversible couples, for mononuclear species, are analyzed in terms of the electrochemical parameterization scheme based upon the $Ru^{III/II}$ couples. Two independent sets of $Re^{II/I}$ potentials are observed, which, if extended, would cross the $Re^{III/II}$ correlation line. The possible significance of these sets is explored. The $Re^{IV/II}$ couple correlation is roughly parallel to one of the $Re^{II/I}$ correlation lines. The analysis leads to some interesting avenues for future synthetic studies.

General Introduction

Recently[1] a ligand electrochemical series was introduced, based upon the $Ru^{III/II}$ couple as an electrochemical standard. Using this series of $E_L(L)$ values, it was shown that many redox couples would fit a linear correlation:

$$E(obs) = S_M[\Sigma E_L(L)] + I_M \qquad (1)$$

where for a given metal and oxidation state, S_M and I_M were constant for all derivatives of given coordination number, stereochemistry and spin state. The sum $[\Sigma E_L(L)]$ is the sum of the $E_L(L)$ values for all ligands binding to the metal ion. Thus a series of linear correlations were presented for various couples, $M^{n+1/n}$, depending on the spin states and relative stereochemistries of M^{n+1} and M^n.

It was noted that, for a very limited data set, pairs of redox couples for the same metal ion had essentially parallel slopes. Thus the S_M values for the couples $Nb^{V/IV}$ and $Nb^{IV/III}$ were identical. Clarke et al.[2] have demonstrated that the correlation lines for $Tc^{IV/III}$, $Tc^{III/II}$ and $Tc^{II/I}$ are also essentially parallel (Figure 1). However $Cr^{III/II}$ (low spin Cr^{II}) is not parallel to[1] $Cr^{I/0}$ and some early work with closely related tris(dithiocarbamato)iron complexes showed that the Fe^{III}/Fe^{II} and Fe^{IV}/Fe^{III} couples were not parallel.[3] Thus the issue is unclear.

This report deals with data for $Re^{IV/III}$, $Re^{III/II}$ and $Re^{II/I}$ in order, in part to explore this issue in more detail, but also to obtain fresh insights into rhenium synthetic chemistry. The rhenium system is more complex than that observed for technetium. Two independent lines are observed for the $Re^{II/I}$ couples and lines for $Re^{III/II}$ and $Re^{II/I}$ if extended, would cross, leading to some interesting synthetic and electrochemical predictions. The $Re^{IV/III}$ line is seen to be approximately parallel to one of the $Re^{II/I}$ lines.

All data are taken from the literature as referenced, and are listed versus NHE. Standard corrections were used where other electrodes were involved.[4] Scatter in the figures may reflect some errors arising from poor reference electrodes, wet solvents or poor electrode design etc., though scatter may also be a consequence of other factors discussed below.

Stereochemistry and Spin state in Rhenium Complexes

The complexes containing the rhenium(I) oxidation state, d^6, are almost invariably low spin and octahedral, but five coordination is possible.[5] Rhenium(II) may exist in low spin, d^5, paramagnetic, six coordinate, mononuclear species or in some dinuclear or cluster species. Rhenium(III), low spin d^4, may be mononuclear six coordinate or seven coordinate,[8-10] or exist in a range of polynuclear species. Finally rhenium(IV), d^3, is commonly six coordinate octahedral,[11] though seven coordinate species are known.[8-9,12-14]

Data Analysis

The literature was explored to find a representatively large selection of $Re^{IV/III}$, $Re^{III/II}$ and $Re^{II/I}$ electrochemically reversible or quasi-reversible couples, recorded in organic solvents (mostly CH_3CN and CH_2Cl_2), and restricted solely to the mononuclear species of these various oxidation states. Oxo species are omitted, as are species involving ligands for which well defined E_L values are not available. All species obtained from the literature and meeting the above requirements are included in the analysis which follows. These data are collected in Table I, and displayed in Figure 2.

A mononuclear rhenium(I) species may gives rise to one to three reversible oxidation couples, while a mononuclear rhenium(IV) species may generate one to three reversible reduction couples. It is entirely possible, for example, that the successive oxidations of a mononuclear rhenium(I) species could lead to a polynuclear rhenium(III) species formed by a following chemical reaction at the electrode. The assumption is made that where a mononuclear species is being investigated, the appearance of electrochemically reversible couples precludes the possible generation of polynuclear species at that couple, on the electrochemical

time scale.

The data are treated in the fashion described earlier[1] to discover the appropriate slope and intercept to describe each couple. From the above discussion, separate linear correlations might be required to describe couples involving six or seven coordinate rhenium(III) (and perhaps rhenium(IV)). If a six coordinate rhenium(II) species oxidizes to six coordinate rhenium(III) and then binds, for example, a supporting electrolyte anion to form a seven coordinate species, this may occur sufficiently slowly on the electrochemical time scale that electrochemical reversibility is observed. In such circumstances the observed potential should fit the correlation for six coordinate species. A six coordinate rhenium(III) species may also rapidly bind a solvent molecule or supporting electrolyte anion to form a seven coordinate rhenium(III) complex. Such a system would fit a different correlation from the standard six coordinate $Re^{III/II}$ correlation (vide infra).

No additional corrections are made in this analysis, except for isocyanide ligands as described below. In general, standard deviations from the best line fits are comparable to those noted for other redox couples in the previous study.[1]

Results

Rhenium(II)/Rhenium(I)

There is a large body of data available for this couple. Some 72 complexes (meeting the above criteria) are included in Table I. However to improve the statistics for this correlation, it was necessary to increase the E_L contributions for isocyanide ligands beyond their normal (uncorrected) values.[1] Isocyanide ligands may bind to metal ions either in a linear or bent manner. When bent, there is an increased back electron donation towards the isocyanide ligand resulting in increased metal-carbon double bond character, and an effective increase in E_L

value.[1,15] In the previous publication, this correction was achieved by adding a term to Eqn.(1) reflecting the number of isocyanide ligands interacting with the HOMO orbital involved in the redox process. In principle this number might vary for every type of isocyanide, and depend upon the degree of bend. However, in practice, it was found acceptable, within the accuracy of the study, only to consider two corrections, one for aromatic isocyanides and one for aliphatic isocyanides (defined for a given metal ion and redox couple).

X-ray data available for some rhenium isocyanide species do indeed demonstrate that some complexes contain bent isocyanide residues.[18-21] However, since X-ray data are not available for all the complexes under consideration, (even if one could assume that the solid and solution phase structures were the same) and since indeed the stereochemistries are not always reported, the data have been fitted in a general fashion except where a specific stereochemistry is known, when the appropriate correction is used.[1] A correction in volts is applied for each aliphatic or aromatic isocyanide ligand multiplied by the number of bound isocyanide ligands to a maximum of 4, being the maximum number of isocyanide ligands interacting with the HOMO orbital even in a hexa-isocyanide species. The actual numerical voltage correction per ligand was obtained by a statistical best fit, within the best 58 complexes [RPhNC 0.22V, MeNC 0.12V].

The most dramatic observation is that there are clearly two independent $Re^{II/I}$ lines, a large data set with ΣE_L above about 1.5 V and a second data set extending up to ΣE_L = 1.5 V with one additional entry at ΣE_L = 2.2 V (Figure 2). The two data sets are also distinguished by the fact that for those in the upper set, in all cases, the bulk species being studied contained six coordinate rhenium(I); thus the first oxidation couple is being plotted. However for the lower data set, the bulk species being studied was almost exclusively six coordinate rhenium(III) and hence the second reduction couple is being plotted. The uppermost member of this lower data set, with ΣE_L = 2.2 V, is a rhenium(II) species in bulk solution.[22]

If the couples are identical in both series, it should not matter what the bulk solution oxidation state is, they should all lie on the same line;[1] that they do not do so, implies some critical difference between these lines.

The statistics for these two lines are shown in Table II. In particular the mean standard deviations (MSD) (calculated minus observed potentials) are only 0.13 and 0.10 V for the upper and lower lines respectively (excluding two very poorly behaved species), comparable to previous data (see footnote to Table II).

Rhenium(III)/Rhenium(II)

Data for 22 complexes are shown in Figure 2 and listed in Table I. The (MSD) is 0.16 V in this case, a little more scattered than the upper $Re^{II/I}$ line. The top end of the line is secured by a set of isocyanide complexes with ΣE_L ca 1.8 V using the same isocyanide correction as found for the $Re^{II/I}$ line (above). These appear to be well defined $Re^{III/II}$ couples.[15] The bottom end of the line is secured by the second reduction potential of the $[Re(NCS)_6]^{2-}$ ion, whose assignment also seems secure.[23-25] The slope (Table II) is near unity but its precise value does depend upon the choice of the isocyanide correction which is not well defined. From a statistical viewpoint a slightly better correlation is obtained by allowing the isocyanide correction to increase to 0.85 V/isocyanide ligand, at which point the slope of the line is about 0.85 being parallel to the $Re^{IV/III}$ line. However such a line passes close to the upper $Re^{II/I}$ line implying that a $Re^{III/II}$ couple should be observed close in potential to the $Re^{II/I}$ couple for species with ΣE_L greater than 1.5. These have not been reported. Moreover such an isocyanide correction seems inordinately large and unlikely.

There is a set of four species with ΣE_L = ca 1.3 - 1.5 which lie well off the line for no obvious reason. These complexes are bis(diphosphine) species and are identified in the Re(III)/Re(II) section of Table II with ##. They are otherwise well behaved species whose $Re^{IV/III}$ and $Re^{II/I}$ couples do lie on their relevant

lines. If one chose to tilt the line so as to include these species, then the points near ΣE_L ca -.4 V and those near 1.8 V would lie well off the line. Moreover the new less steep line would be much poorer, statistically, than the current line and would cut through negative of the $Re^{II/I}$ line. This would lead to the expectation of observing $Re^{III/I}$ two-electron couples which are generally not observed. Thus a more consistent interpretation of the data places the line as shown in Figure 2, but leaves the behaviour of the four points unexplained. Conceivably, in these four cases, the $Re^{III/II}$ species in solution is seven coordinate by reaction with a counter or electrolyte anion. This would certainly cause a shift to more negative potential. However this might also be expected to shift the $Re^{IV/III}$ couple off its line, and yet these points are well behaved.

Certainly if one were to suppose that the rhenium(IV)/rhenium(III) {seven coordinate} correlation was in fact very similar to the six coordinate correlation reported here, then the scatter in the $Re^{III/II}$ line might arise because it is in fact two lines (one for six coordinate Re^{III} and one for seven coordinate Re^{III}), which are not resolved here. The seven coordinate Re^{III} line would lie lower than the six coordinate Re^{III} line and might run through [Re(bpy)Cl_4 and the four poorly behaved species, cutting negative of the $Re^{II/I}$ (upper) line. This is a speculative hypothesis for the moment awaiting more data and detailed consideration of the reasonable possibility that some six coordinate rhenium(III) species may bind an electrolyte anion (or perhaps solvent) in the electrochemical cell. Certainly such an equilibrium has been observed when additional more strongly binding ligands are present;[8] see further comment below.

Rhenium(IV)/Rhenium(III)

This couple was discussed in the previous report (Figure 9),[1] and is extended in this contribution (Figure 2). It is a well behaved couple with all available data lying on one line with little scatter. The slope of this line is similar to that of the $Tc^{IV/III}$ line with an intercept slightly less positive.[2]

Discussion

As shown in Figure 2, the $Re^{II/I}$ upper line if extended to more negative ΣE_L would likely cut through the $Re^{III/II}$ line. If it did, then all rhenium(III) couples with ΣE_L more negative than the crossing would thermodynamically be required to be two-electron $Re^{III/I}$ events. These are not observed in this region. The appearance of the lower $Re^{II/I}$ correlation avoids this situation by interposing a discontinuity such that the upper $Re^{II/I}$ correlation evidently ceases to exist before it crosses the $Re^{III/II}$ line.

This must have structural or bonding significance, but there are no additional data available to define just how these rhenium(I) species formed at such negative potentials, differ from those on the upper $Re^{II/I}$ line which are much more stable towards oxidation.

The only reasons which have been identified which would lead to two different lines for the same couple would be differing spin states and/or stereochemistries or coordination numbers. Considering the upper $Re^{II/I}$ line, certainly the bulk starting materials in this data set are all six coordinate low spin rhenium(I). Few rhenium(II) oxidation products (with $\Sigma E_L \geq 2.0$) have been isolated, but one has been identified as low spin six coordinate rhenium(II),[20] and another has been similarly characterized by X-ray structural analysis;[21] thus the upper line most likely represents the low spin six coordinate $Re^{II/I}$ couple.

Heavy transition elements such as rhenium are expected to be low spin, but if any high spin species were to be observed, then they would occur with smaller ΣE_L values since such values are derived from ligands which are good σ and π-electron donors, a situation favoring high spin behaviour. It is inconceivable that d^6 Re^I would become high spin, but more likely that d^5 Re^{II} could become high spin given the much larger exchange stabilization of this spin state.

This possibility is however excluded because:-

i) One member of the lower group contains 2 CO ligands; it is unreasonable to expect such a species to be high spin.

ii) A big shift to negative potentials, from the upper line to the lower line, requires a significant destabilization of rhenium(I) or stabilization of rhenium(II) (relative to the upper line complexes). A switch to high spin Re^{II} would provide the opposite effect.

iii) A reduced slope also implies relatively weaker binding to rhenium(I).

Rejecting a change in spin state for the lower line, leaves only a change in stereochemistry or coordination number. The bulk species being studied in this region are all six coordinate rhenium(III) or rhenium(II). It is possible that the rhenium(I) species being formed is five coordinate since such rhenium(I) species are known.[5] However any reasonable argument would predict that oxidation of a five coordinate rhenium(I) species to a six coordinate rhenium(II) species would occur at more positive potentials than oxidation of the corresponding six coordinate rhenium(I) species,[1] which is not the case under consideration. Moreover it is hard to believe that the successive reduction of a six coordinate rhenium(III) species to a five coordinate rhenium(I) species, thereby losing a ligand, would be electrochemically reversible.

Possibly the rhenium(I) species has changed from octahedral to trigonal prismatic. Such a stereochemistry is well established for rhenium(V) and rhenium(VI) species,[27-29] but not previously observed for low oxidation state rhenium. Such a change might well be facile enough to retain electrochemical reversibility. A final answer must await some spectroscopic or structural studies of these difficult to obtain rhenium(I) species.

So far all correlations with ΣE_L have been linear, but one cannot exclude the possibility that the binding characteristics of a metal ion, however they may be defined, might change over a large range of E_L such that a curved relationship is

found. Possibly that is the case with the Re^{II}/Re^{I} relationship. It is possible to fit a non-linear relationship such as that shown, as an example, in Figure 2 (dotted line).[30] Quite a few points lie well off this line so that statistically it is not very successful.

Crossing of $Re^{III/II}$ and lower $Re^{II/I}$ Lines

Previous pairs of redox couples, for the same metal ion in different oxidation states are either essentially parallel or, if not, would cross one another in chemically nonsensical ΣE_L regions. For example, the $Tc^{III/II}$ and $Tc^{II/I}$ lines are close to parallel; they would cross near ΣE_L = ca 19 V. The rhenium data are then especially interesting in that the upper and lower $Re^{II/I}$ lines might cross the $Re^{III/II}$ line in an accessible ΣE_L region. Evidently the existence of the lower $Re^{II/I}$ line precludes the upper crossing, i.e. the crossing is avoided. Yet it is still possible that the lower $Re^{II/I}$ line will cross the $Re^{III/II}$ line, apparently near ΣE_L ca -0.5 V, with some uncertainty because of the poor statistics of both the lower $Re^{II/I}$ line and the $Re^{III/II}$ line.

Clearly there is some interesting chemistry to explore with rhenium species whose ΣE_L is near -0.5 V or more negative. For example, the reduction chemistry of the $[ReX_6]^{2-}$ ions (X = halides, pseudohalides etc) would bear further exploration.

Seven coordinate rhenium(III) couples

The species mer-$ReCl(CO)_3(PMe_2Ph)_2$ (ΣE_L = 3.41 V) exhibits a two-electron oxidation process,[14,31] at $E_{1/2}$ = 1.40 V, apparently terminating with the seven coordinate $ReCl_3(CO)_2(PMe_2Ph)_2$ species. In this particular case, the two-electron process is probably driven by the formation of this seven coordinate rhenium(III) species which evidently undergoes a $Re^{III/II}$ oxidation process at potentials less positive than the calculated $Re^{II/I}$ couple of the starting material (1.63 V)[14-32] (Figure 2). Such a two-electron process is not expected, nor yet reported, if the

final product is a six coordinate rhenium(III) species. This observation is consistent with the hypothesis above that the extension of a Re^{III}{seven coordinate}/Re^{II} line might cut through the $Re^{II/I}$ upper line.

The oxidation of seven coordinate $ReCl_3(CO)(PMe_2Ph)_3$ has been reported to be fairly reversible.[22] The observed potential is almost exactly that predicted by the $Re^{IV/III}$ correlation if ΣE_L for the seven ligands is used, but the calculation cannot be that simple and the agreement is probably fortuitous.

Slope Analysis

The electrode potential depends upon many factors including metal-ligand binding free energies and, differential solvation (the difference between the solvation free energies of the oxidized and reduced species).[33] The fact that, in organic solvents, the overall charge on the complex does not seem to be an important factor, may suggest that in many organic solvents the differential solvation term largely vanishes. However, given the relatively large magnitude of the solvation terms, it is rather surprising that a +/0 species, for example, would fit the same line as a +4/+3 species. Nevertheless they appear to do so. Possibly the binding free energies are modified by these charges such that there is a levelling effect as the charge changes. As ΣE_L increases, the potential becomes more positive, and the free energy of metal-ligand binding to the lower oxidation state is becoming progressively larger than that of the higher oxidation state.

The slope of the upper $Re^{II/I}$ line is 0.76, relative to unity for the $Ru^{III/II}$ data. Thus relative to ruthenium, the rhenium data show that with increasing ΣE_L, the lower oxidation state while still progressively favoured, does not increase in stability to the same degree as Ru^{II}. The slope of this line is also very significantly less than that for the corresponding $Tc^{II/I}$ line (Table II). Given that the E_L scale is basically one in which E_L values increase with decreasing

availability of σ-electron density, and/or increasing π-acceptor ability, then these results show that such ligands favour binding to technetium(I) (relative to technetium(II)) to a greater degree than rhenium(I) (relative to rhenium(II)). Similarly, electron rich and π-donor ligands favour binding to rhenium(I) to a greater degree than technetium(I).

The slope of the $Re^{III/II}$ line, albeit less well defined, is certainly less than that for the corresponding $Tc^{III/II}$ line. Previously it had been noted that technetium(III) complexes had reduction couples about 0.2 V more positive than the corresponding rhenium(III) species.[34] It is now seen that this is only true for complexes of relatively large ΣE_L. The $Re^{III/II}$ line crosses the $Tc^{III/II}$ line near $\Sigma E_L = 0.1$;[35] below this value, the rhenium complex will have the higher redox potential.

Final Comments

Data have been reported in this study for 119 redox couples displayed in Figure 2. Allowing that agreement between calculated and observed of < 0.25 V represents good behavior, only 9 redox couples are poorly fitted, possibly 3 for reasons of experimental error, and 6 for more subtle reasons.[37] Certainly most of the data reported here fit predicted potentials to within 0.15 V (Table II).

The appearance of a pair of lines for the $Re^{II/I}$ redox couple is unexpected; the observation suggests some important structural or electronic differences between the rhenium(I) species in the upper and lower lines. However the possibility that the Re^{II}/Re^{I} line is really a curve cannot be excluded. It is therefore desirable to obtain data for ΣE_L values in the intermediate range between the two lines. Such data should provide better statistics for the lower line or

disprove the discontinuity. If two lines are present then physical data are need to define the differences between the complexes on each line.

Study of the electrochemistry of definitive seven coordinate rhenium(III) species is clearly desirable. Some reversible electrochemistry has been observed with seven coordinate hydride rhenium species.[13,38] Controlled potential reduction studies of rhenium species of negative ΣE_L values should prove especially interesting.

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Figure Legends

Figure 1 Correlation lines for $Tc^{IV/III}$, $Tc^{III/II}$ and $Tc^{II/I}$. Reproduced from Reference[2] with permission of the Authors and the American Chemical Society.

Figure 2 Correlations lines for a) upper and lower $Re^{II/I}$ couples, b) $Re^{III/II}$ couple; the four closed triangles refer to the four poorly behaved complexes discussed in the text. and c) $Re^{IV/III}$ The point designated by a reversed closed triangle corresponds with the 2-electron oxidation of m-$ReCl(CO)_3(PMe_2Ph)_2$. All data in Volts vs NHE. See Table I for the observed and calculated data.

Table I

Data presentation for Figures 2. Comparison of Observed and Calculated Potentials in Volts vs. NHE.[a]

Ref.	Complex	Obs.	Cal.	ΣE_L
<u>Rhenium(II)/Rhenium(I) (lower line)</u>				
[34,36]	Re(dmpe)$_2$Cl$_2$ (1+)	-1.36	-1.26	0.64
[23]	Re(NCS)$_3$(PEt$_2$Ph)(bpy)	-1.26	-1.25	0.68
[23]	Re(NCS)$_3$(PEt$_2$Ph)(phen)	-1.24	-1.25	0.68
[34]	Re(dmpe)$_2$Br$_2$ (1+)	-1.22	-1.25	0.68
[34]	Re(diars)$_2$Cl$_2$ (1+)	-1.25	-1.20	0.88
[23]	Re(NCS)$_3$(PEt$_2$Ph)(dppe)	-1.11	-1.19	0.92
[34]	Re(dppe)$_2$Cl$_2$ (1+)	-1.00	-1.18	0.96
[6]	Re(Cl$_2$)(CN-^{i}Pr)$_2$(PMePh$_2$)$_2$	-0.96	-1.11	1.22
[39]	Re(ophen(PPh$_2$)$_2$)$_2$Cl$_2$	-1.22	-1.08	1.32
[40]	Re(dppee)$_2$Cl$_2$ (1+)	-1.20	-1.03	1.48
[40]	Re(dppee)$_2$Br$_2$ (1+)	-1.08	-1.02	1.52
[22]	ReCl$_2$(CO)$_2$(P^{n}Pr$_3$)$_2$	-0.75	-0.84	2.22
<u>Rhenium(II)/Rhenium(I) (upper line)</u>				
[41]	t-Re(N$_2$)(dtc)(PMe$_2$Ph)$_3$	-0.02	0.21	1.54
[15]	Re(CNCMe$_3$)(dppe)$_2$Cl	0.30	0.32	1.68
[15]	Re(CNMe)(dppe)$_2$Cl	0.32	0.33	1.69
[41]	t-Re(N$_2$)Cl(Py)(PMe$_2$Ph)$_3$	0.15	0.34	1.71
[41]	Re(N$_2$)Br(Py)(PMe$_2$Ph)$_3$	0.19	0.36	1.74
[15]	Re(CNPh,4-OMe)(dppe)$_2$Cl	0.43	0.39	1.78
[15]	Re(CNPh,2-Me)(dppe)$_2$Cl	0.50	0.39	1.78

[15]	Re(CNPh,4-Me)(dppe)$_2$Cl	0.48	0.40	1.79
[15]	Re(CNPh,4-Cl)(dppe)$_2$Cl	0.54	0.41	1.80
[41]	t-Re(N$_2$)Cl(PMe$_2$Ph)$_4$	0.29	0.41	1.80
[42]	Re(dppe)$_2$Cl(CNPh)	0.51	0.43	1.83
[15]	Re(CNPh,2,6-Cl$_2$)(dppe)$_2$Cl	0.67	0.47	1.88
[15,43]	Re(N$_2$)(dppe)$_2$Cl	0.52	0.47	1.88
[21]	Re(CNCMe$_3$)$_2$(Py)(NCMe)(PPh$_3$)$_2$	0.41	0.63	2.09
[41]	Re(CO)Cl(PMe$_2$Ph)$_4$	0.65	0.64	2.11
[43]	t-Re(N$_2$)Cl(P(OMe)$_3$)$_4$	0.66	0.65	2.12
[21]	Re(CNCMe$_3$)$_2$(NCMe)$_2$(PPh$_3$)$_2$	0.48	0.70	2.18
[42]	Re(dppe)$_2$Cl(CO)	0.92	0.70	2.19
[15]	Re(CNMe)(NCMe)(dppe)$_2$ (1+)	0.87	0.76	2.27
[44]	Re(CNCMe$_3$)$_2$(dppe)$_2$ (1+)	1.04	0.86	2.40
[42]	Re(CNMe)(CNCMe$_3$)(dppe)$_2$ (1+)	1.03	0.87	2.41
[15]	Re(CNMe)$_2$(dppe)$_2$ (1+)	1.03	0.88	2.42
[41]	Re(N$_2$)Cl(CO)(PMe$_2$Ph)$_3$	0.81	0.90	2.45
[45]	Re(terpy)(CO)$_2$Cl ##	1.43	0.93	2.49
[46]	Re(CNPh,4-Me)$_5$Cl	0.74	0.93	2.49
[46]	Re(CNPh,4-Me)$_5$Br	0.75	0.95	2.51
[15]	Re(CNMe)(CNPh,4-Me)(dppe)$_2$ (1+)	1.07	0.95	2.52
[15]	Re(CNMe)(CNPh,4-Cl)(dppe)$_2$ (1+)	1.10	0.96	2.53
[15]	Re(CNMe)(CNPh)(dppe)$_2$ (1+)	1.09	0.98	2.56
[16]	Re(CNCMe$_3$)$_4$(PEt$_3$)$_2$ (1+)	0.87	1.01	2.60
[43]	Re(N$_2$)(NCMe)(dppe)$_2$+	1.03	1.02	2.61
[44]	Re(dppe)$_2$(CNPh,4-Me)$_2$	1.17	1.03	2.62
[44]	Re(dppe)$_2$(CNPh,4-MeO)$_2$	1.12	1.03	2.62
[43]	Re(N$_2$)Cl(CO)((P(OMe)$_3$)(PPh$_3$)$_2$	0.93	1.04	2.63
[16]	Re(CNCMe$_3$)$_6$ (1+)	0.98	1.04	2.64

[44]	$Re(dppe)_2(CNPh,4\text{-}Cl)_2$	1.22	1.04	2.64
[43]	$Re(N_2)Cl(CO)((P(OMe)_3)_3$	1.05	1.08	2.69
[16]	$Re(CNCMe_3)_4(PPh_3)_2$ (1+)	1.05	1.09	2.70
[43]	$Re(N_2)(NCPh)(dppe)_2$ (1+)	1.15	1.13	2.75
[14]	$ReCl(CO)_2(PMe_2Ph)_3$	1.06	1.13	2.76
[44]	$Re(dppe)_2(CNPh,2,6\text{-}Cl_2)_2$	1.29	1.16	2.80
[15]	$Re(CNMe)CO(dppe)_2$ (1+)	1.39	1.26	2.92
[47]	c-$Re(bpy)_2(CO)_2$ (1+)	1.12	1.33	3.02
[46]	$Re(CNPh,4\text{-}OMe)_6$ (1+)	1.34	1.35	3.04
[46]	$Re(CNPh,4\text{-}Me)_6$ (1+)	1.44	1.39	3.10
[47]	t,c-$Re(bpy)(PMe_2Ph)_2(CO)_2$ (1+)	1.34	1.45	3.18
[48]	$Re(4,4Me_2\text{-}bpy)(CO)_3Cl$	1.49	1.46	3.19
[49]	$Re(N_2)Cl(CO)_2(PPh_3)_2$	1.25	1.47	3.20
[50]	f-$Re(phen)(CO)_3Cl$	1.57	1.51	3.25
[46]	$Re(CO)(CNMe)_5$ (1+)	1.42	1.56	3.32
[45]	$Re(4,4NO_2bpy)(CO)_3Cl$	1.72	1.57	3.33
[22]	t-$ReCl(CO)_3(PMe_2Ph)_2$	1.42	1.63	3.41
[51]	$Re(Cl)(CO)_3(NCMe)_2$	1.70	1.63	3.41
[44]	$Re(CO)_2(dppe)_2$ (1+)	1.66	1.63	3.42
[52]	m-$Re(CO)_3(P\text{-}mtol_3)_2Cl$	1.69	1.67	3.47
[52]	m-$Re(CO)_3(PPh_3)_2Cl$	1.69	1.70	3.51
[52]	m-$Re(CO)_3(P\text{-}mtol_3)_2Br$	1.63	1.72	3.53
[46]	c-$Re(CO)_2(MeNC)_4$ (1+)	1.94	1.85	3.70
[48]	$Re(bpy)(CO)_3(4\text{-}EtPy)$ (1+)	2.09	1.88	3.72
[46]	$Re(CNPh,4\text{-}Me)_5(CO)$ (1+)	1.65	1.88	3.72
[46]	m-$Re(CO)_3(CNMe)_3$ (irreversible)[b]	2.45	2.41	4.44
[51]	f-$Re(CO)_3(NCMe)_3$ (1+) ##	1.57	2.06	3.99

Rhenium(III)/Rhenium(II)

[23]	$Re(NCS)_6$ (3-)	-1.39	-1.30	-0.36
[47]	$Re(bpy)Cl_4$	-1.02	-1.39	-0.44
[53]	$ReCl_4(CNPh)_2$ (1-)	-0.48	-0.71	0.14
[47]	f-$Re(bpy)(PMe_2Ph)Cl_3$	-0.50	-0.71	0.14
[47]	f-$Re(bpy)(PPh_3)Cl_3$	-0.46	-0.66	0.19
[54]	$ReCl_3(PMe_2Ph)_3$	-0.69	-0.53	0.30
[47]	m-$Re(PPh_3)_2(NCMe)Cl_3$	-0.60	-0.41	0.40
[36]	$Re(dmpe)_2Cl_2$ (1+)	-0.19	-0.13	0.64
[23]	$Re(NCS)_3(PEt_2Ph)(phen)$	-0.14	-0.08	0.68
[34]	$Re(dmpe)_2Br_2$ (1+)	-0.10	-0.08	0.68
[23]	$Re(NCS)_3(PEt_2Ph)(bpy)$	-0.14	-0.08	0.68
[47]	t,c-$Re(bpy)(PMe_2Ph)_2Cl_2$ (1+)	-0.15	-0.04	0.72
[34]	$Re(diars)_2Cl_2$ (1+)	-0.12	0.15	0.88
[23]	$Re(NCS)_3(PEt_2Ph)(dppe)$	-0.10	0.15	0.88
[34]	$Re(dppe)_2Cl_2$ (1+)	-0.01	0.25	0.96
[6]	$ReCl_2(CN^iPr)_2(PMePh_2)_2$ (1+)	0.05	0.27	0.98
[39]	$Re(ophen(PPh_2)_2)_2Cl_2$ (1+) ##	-0.08	0.67	1.32
[39]	$Re(ophen(PPh_2)_2)_2Br_2$ (1+) ##	0	0.71	1.36
[40]	$Re(dppee)_2Cl_2$ (1+) ##	-0.03	0.85	1.48
[40]	$Re(dppee)_2Br_2$ (1+) ##	0.06	0.90	1.52
[15]	$Re(CNCMe_3)(dppe)_2Cl$	1.22	1.09	1.66°
[15]	$Re(CNMe)(dppe)_2Cl$	1.23	1.10	1.69°
[15]	$Re(CNPh,4\text{-}OMe)(dppe)_2Cl$	1.28	1.20	1.76°
[15]	$Re(CNPh,4\text{-}Me)(dppe)_2Cl$	1.34	1.21	1.79°
[15]	$Re(CNPh,2\text{-}Me)(dppe)_2Cl$	1.33	1.21	1.79°
[15]	$Re(CNPh,2,6\text{-}Cl_2)(dppe)_2Cl$	1.46	1.32	1.86°

Rhenium(IV)/Rhenium(III)

[55]	$ReCl_6$ (4-)	-0.88	-0.73	-1.44
[56]	$ReBr_6$ (4-)	-0.68[d]	-0.62	-1.32
[47]	$Re(bpy)Cl_4$	0.20	0.13	-0.44
[23,24]	$Re(NCS)_6$ (4-)	0.13	0.20	-0.36
[51]	c-$Re(NCMe)_2Cl_4$	0.24	0.27	-0.28
[54]	$ReCl_4(PMe_2Ph)_2$	0.10	0.27	-0.28
[47]	f-$Re(bpy)(PMe_2Ph)Cl_3$	0.71	0.62	0.14
[53]	$ReCl_4(CNPh)_2$ (1-)	0.77	0.63	0.14
[57]	$ReCl_3$(Tetrahydrothiophene)$_3$	0.86	0.66	0.18
[47]	f-$Re(bpy)(PPh_3)Cl_3$	0.80	0.67	0.19
[57]	$ReBr_3$(Tetrahydrothiophene)$_3$	0.87	0.71	0.24
[54]	$ReCl_3(PMe_2Ph)_3$	0.88	0.76	0.30
[47]	m-$Re(PPh_3)_2(NCMe)Cl_3$	0.90	0.85	0.40
[23]	$Re(NCS)_3(PEt_2Ph)(bpy)$	0.92	1.09	0.68
[23]	$Re(NCS)_3(PEt_2Ph)(bpy)$	0.92	1.09	0.68
[47]	t,c-$Re(bpy)(PMe_2Ph)_2Cl_2$ (1+)	1.12	1.12	0.72
[23]	$Re(NCS)_3(PEt_2Ph)(dppe)$	1.06	1.26	0.86
[39]	$Re(ophen(PPh_2)_2)_2Cl_2$ (1+)	1.71	1.64	1.32
[39]	$Re(ophen(PPh_2)_2)_2Br_2$ (1+)	1.68	1.67	1.36
[40]	$Re(dppee)_2Cl_2$ (1+)	1.75	1.77	1.46
[40]	$Re(dppee)_2Br_2$ (1+)	1.71	1.81	1.52

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a) For abbreviations, see ref.[1]; dppee = cis-1,2-bis(diphenylphosphino)ethene. The charges indicated after some species refer to the charge on the bulk species being studied; if no charge is indicated, the bulk species is electrically neutral. The calculated data reported here were obtained from a Lotus[tm] programme prior to rounding off the slope and intercept to 2 decimal places. The numbers shown here

may therefore not always agree exactly with those obtained using the equations in Table II. ## identifies poor agreement between observed and calculated, error > 0.4 V. These entries were not included in the linear regression analysis. b) Not included in linear regression analysis. c) These isocyanide ΣE_L value contain the same correction factor as determined to best fit the $Re^{II/I}$ data. d) Both the $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ ions were initially reported to have irreversible $Re^{IV/III}$ couples.[58] More recent studies on the $[ReCl_6]^{2-}$ reported a reversible couple at essentially the same potential.[55] Thus the value reported here for $[ReBr_6]^{2-}$ is likely correct; it was not, however, included in the linear regression analysis.

Table II

Correlation Data for Rhenium and Technetium Couples[a]

Couple	S_M	I_M	R	MSD[b,c] V	#[d] >0.25 V	N[e] >0.15 <0.25 V	#[f]
$Re^{II/I}$ (upper)	0.76(.03)	-0.95(.13)	0.96	0.134	2	17	59[g]
(lower)	0.27(.07)	-1.43(.11)	0.76	0.104	0	2	12
$Re^{III/II}$	1.17(.06)	-0.88(.17)	0.97	0.188	3	7	22[h]
$Re^{IV/III}$	0.86(.04)	0.51(.13)	0.98	0.124	0	6	20
$Tc^{II/I}$	1.42(.12)	-2.09(.10)	0.94				14
$Tc^{III/II}$	1.28(.08)	-0.89(.11)	0.86				22
$Tc^{IV/III}$	1.00(.04)	0.65(.09)	0.92				12

a) S_M and I_M are the slope and intercept of Eqn.1, R is the correlation coefficient; standard deviations of slope and intercept are given in parenthesis in volts. b) MSD is the standard deviation in volts of calculated minus observed potential. c) For comparison, previous MSD values include $Cr^{III/II}$(LS) 0.120, $Cr^{II/I}$ 0.115, $Fe^{III/II}$(LS) 0.109, $Mn^{II/I}$ 0.079, $Mo^{I/0}$ 0.095, $Os^{III/II}$ 0.099 and $Ru^{III/II}$ 0.035 V.[1] d) Number of data points deviating by more than 0.25 V from calculated value. e) Number of data points deviating by more than 0.15 V but less than 0.25 V. f) Total Number of data points used in the correlation. The technetium data are taken from ref.[2] g) Excludes two very poorly behaved points.[37] h) Excludes four very poorly behaved points, see text.

Bibliography

1. Lever, A. B. P. Inorg. Chem, 1990, 29, 1271-85.

2. Lu, J.; Yaman, A.; Clarke, M. J. Inorg.Chem., 1990, 29, 3483.

3. Chant, R.; Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. Inorg.Chem., 1975, 14, 1894.

4. Bard, A. J.; Faulkner, R. Electrochemical Methods: Fundamentals and Applications, Wiley-interscience, New York, NY 1980

5. Hughes, D. L.; Pombeiro, A. J.; Pickett, C. J.; Richards, R. L. J.Organomet.Chem., 1983, 248, C26.

6. Warner, S.; Lippard, S.J. Inorg.Chem., 1989, 28, 3008-13.

7. Farr, J. L.; Abrams, M. J.; Costello, C. E.; Davison, A.; Lippard, S. J.; Jones, A. G. Organometallics, 1985, 4, 139.

8. Treichel, P. M.; Williams, J. P.; Freeman, W. A.; Gelder, J. I. J.Organomet.Chem., 1979, 170, 247.

9. Drew, M. G. B.; Davis, K. M.; Edwards, D. A.; Marshalsea, J. J. Chem. Soc. Dalton, 1978, 1098.

10. Fletcher, S. R.; Skapski, A. C. J. Chem. Soc. Dalton, 1974, 486.

11. Rouschias, G. Chem.Rev., 1974, 74, 531.

12. Ichimura, A.; Yamamoto, Y.; Kajino, T.; Kitagawa, T.; Kuma, H.; Kushi; Y. Chem.Commun., 1988, 1130.

13. Moehring, G. A.; Walton, R. A. J. Chem. Soc. Dalton, 1987, 715.

14. Seeber, R.; Mazzocchin, G.A.; Mazzi, U.; Roncari, E.; Refosco, F. Trans.Met.Chem. (Weinheim), 1984, 9, 315-318.

15. Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. J.Organomet.Chem., 1982, 224, 285-294.

16. Allison, J. D.; Wood, T. E.; Wild, R.E.; Walton, R. A. Inorg.Chem., 1982, 21, 3540-3546.

17. Carvalho, F. N. N.; Pombeiro, A. J. L.; Orama, O.; Schubert, U.; Pickens, C. J.;

Richards, R. L. J.Organomet.Chem., 1982, 240, C18.

18. Chiu, K. W.; Howard, C. G.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. Polyhedron, 1982, 1, 803.

19. Pombeiro, A. J. L.; Hitchcock, P. B.; Richards, R. L. Inorg. Chim. Acta, 1983, 76, L225-L226 75.

20. Fernanda, M.; Carvalho, N. N.; Pombeiro, A. J. 1.; Schubert, U.; Orama, O.; Pickett, C. J.; Richards, R. L. J. Chem. Soc. Dalton, 1985, 2079-84.

21. Allison, J. D.; Fanwick, P. E.; Walton, R. A. Organometallics, 1984, 3, 1515-20.

22. Dunbar, K. R.; Walton, R. A. Inorg.Chim.Acta, 1984, 87, 185-91.

23. Hahn, J. E.; Nimry, T.; Robinson, W. R.; Salmon, D. J.; Walton, R. A. J. Chem. Soc. Dalton, 1978, 1232-36.

24. Hurst, R. W.; Heineman, W. R.; Deutsch, E. Inorg.Chem., 1981, 20, 3298-303.

25. Trop, H. S.; Davison, A.; Jones, A. G.; Davis, M. A.; Szalda, D. J.; Lippard, S. J. Inorg.Chem., 1980, 19, 1105.

26. Pombeiro, A. J. Personal communication 1990.

27. Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J., Transition Met. Chem, 1982, 7, 353.

28. Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Nicholson, T.; Zubieta, J. J. Chem. Soc., Dalton Trans, 1986, 1339-45.

29. Kirmse, R.; Stach, J.; Spies, H. Inorg. Chim. Acta, 1980, 45, L251-L253.

30. The dotted line curved correlation shown in Figure 2 has the equation E = 1.84 Ln(E_L(L)) - 0.695, obtained by a best fit of all data points less the group of points on the lower line positive of E_L(L) = 1.0.

31. Seeber, R.; Mazzocchin, G. A.; Roncari, E.; Mazzi, U. Transition Metal Chem., 1981, 6, 123-4.

32. The calculated value is based on the E_L(L) value for the six coordinate species, and using the $Re^{II/I}$ (upper) correlation. This is appropriate since this oxidation will occur before the complex binds a seventh ligand and oxidises

further. The authors note that under some experimental circumstances, it is possible to see both the $Re^{II/I}$ and $Re^{III/II}$ processes occurring at very similar potentials.

33. Richardson, D. E. Inorg.Chem., 1990, 29, 3213-17.

34. Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. Inorg.Chem., 1987, 26, 3108-3113.

35. Due to uncertainty in the exact slope of the $Re^{III/II}$ correlation, this intercept value can only be considered approximate.

36. Vanderheyden, J-L.; Heeg, M. J.; Deutsch, E. Inorg.Chem., 1985, 24, 1666-73.

37. The four poor $Re^{III/II}$ couples have already been discussed. The $Re^{II/I}$ couple for the species [Re(terpy)(CO)2Cl] [terpy = 2,2',2"-terpyridine][45] is too high by 0.5 V and that for[51] f-Re(CO)3(NCMe)3, too low, by 0.5 V for no obvious reasons.

38. Fanwick, P. E.; Leeaphon, M.; Walton, R. A. Inorg.Chem., 1990, 29, 676.

39. Esjornson, D.; Bakir, M.; Fanwick, P. E.; Jones, K. S.; Walton, R. A. Inorg.Chem., 1990, 29, 2055.

40. Bakir, M.; Fanwick, P. E.; Walton, R. A. Polyhedron, 1987, 6, 907-13.

41. Chatt, J.; Elson, C. M.; Hooper, N. E.; Leigh, G. J. J. Chem. Soc. Dalton, 1975, 2392.

42. Fernanda, M.; Carvalho, N. N.; Pombeiro, A. J. L. J. Chem. Soc. Dalton, 1989, 1209-16.

43. Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. Inorg.Chem., 1987, 26, 2674-2683.

44. Pombeiro, A. J. L. Inorg.Chim.Acta, 1985, 103, 95-103.

45. Juris, A.; Campagna, S.; Bidd, I.; Lehn, J-M.; Ziessel, R. Inorg.Chem., 1988, 27, 4007-4011.

46. Treichel, P. M.; Williams, J. P. J.Organomet.Chem., 1977, 135, 39-51.

47. Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. Inorg.Chem., 1984, 23, 2104-2109.

48. Meyer, T. J. personal letter, 1989.

49. Leigh, G. J.; Morris, R. H.; Pickett, C. J.; Stanley, D. R.; Chatt, J. J. Chem. Soc. Dalton, 1981, 800.

50. Luong, J. C.; Nadjo, L.; Wrighton, M. S. J.Am.Chem.Soc., 1978, 100, 5790.

51. Brisdon, B. J.; Edwards, D. A.; Towell, I. M.; Moehring, G. A.; Walton, R. A. J. Chem. Soc. Dalton, 1988, 245.

52. Bond, A. M.; Colton, R.; McDonald, M. E. Inorg.Chem., 1978, 17, 2842-47.

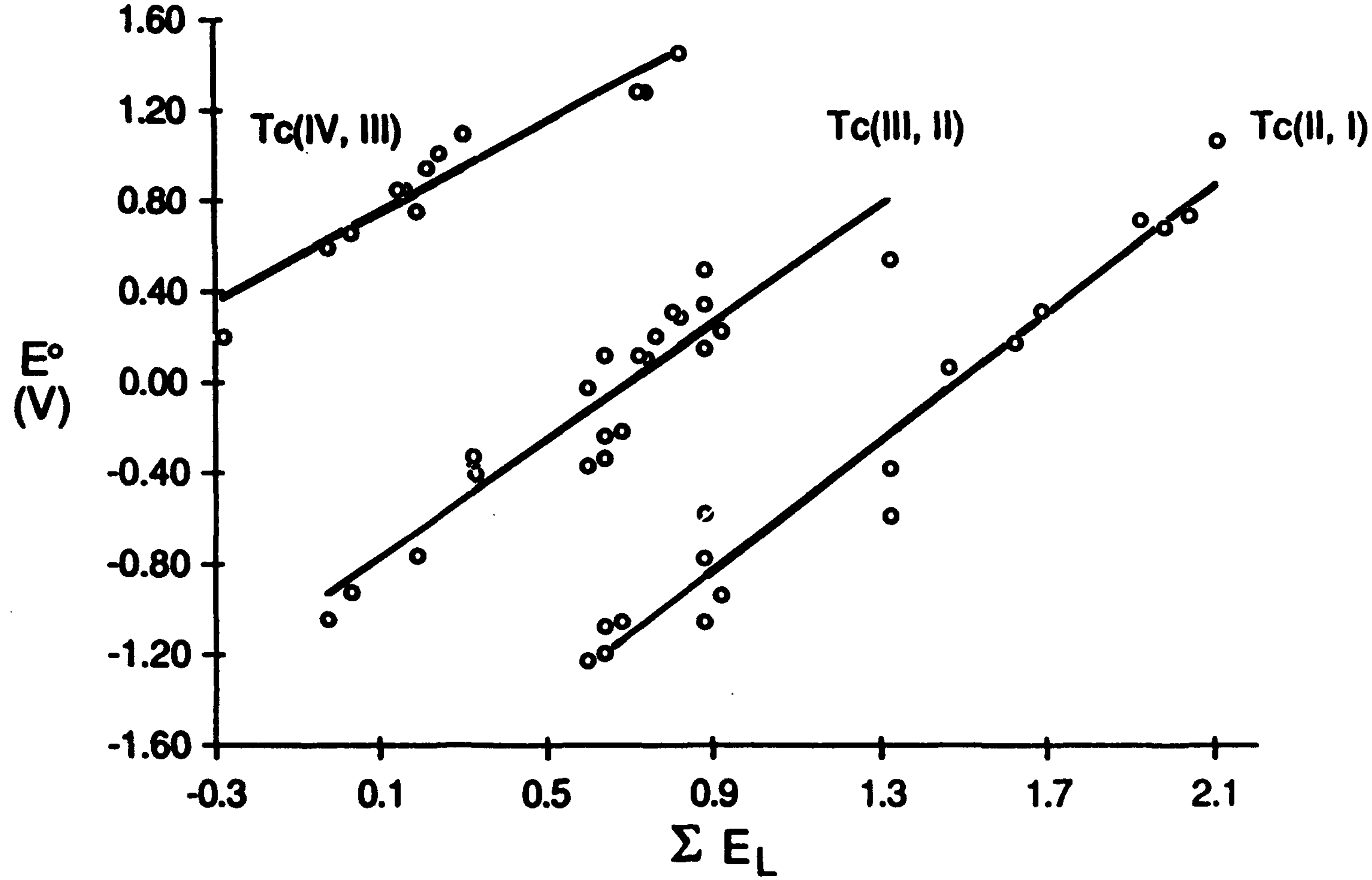
53. Cameron, C. J.; Tetrick, S. M.; Walton, R .A. Organometallics, 1984, 3, 240-47.

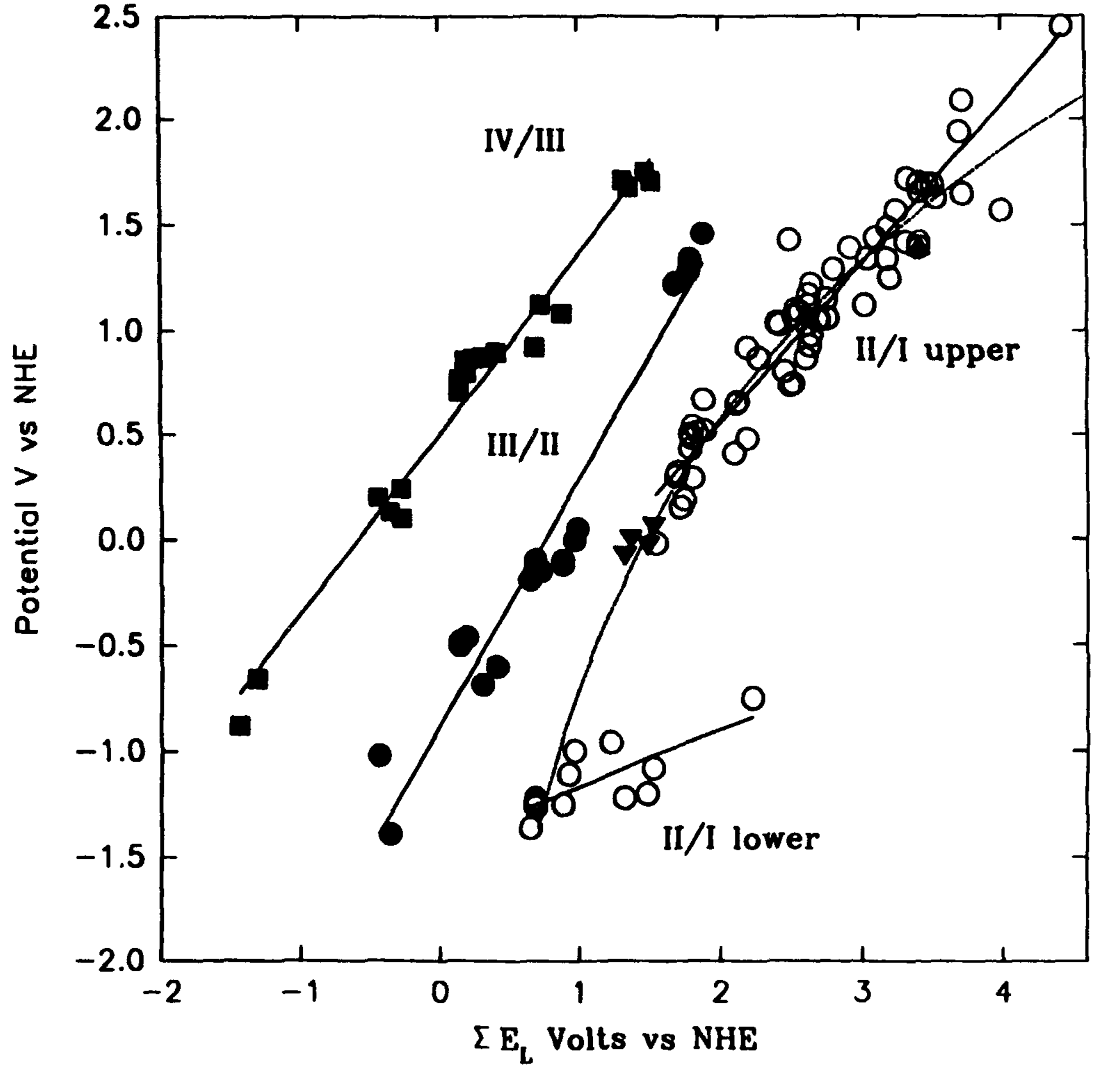
54. Roncari, E.; Mazzi, U.; Seeber, R.; Zanello, P. J.Electroanal.Chem., 1982, 132, 221-31.

55. Heath, G. A.; Moock, K. A.; Sharp, D. W. A.; Yellowlees, L. J. Chem.Commun., 1985, 1503-05.

56. Trop, H. S.; Davison, A.; Carey, G. H.; DePamphilis, B. V.; Jones, A. G.; Davis, M. A. J.Inorg.Nucl.Chem., 1979, 41, 271-2.

57. Gardiner, I. M.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. Inorg.Chem., 1989, 28, 3688-95.


1.60
1.20
0.80
0.40
0.00
-0.40
-0.80
-1.20
-1.60
E°
(V)
Tc(IV, III)
Tc(III, II)
Tc(II, I)
-0.3
0.1
0.5
0.9
1.3
1.7
2.1
Σ E$_L$



IV/III
III/II
II/I upper
II/I lower
Potential V vs NHE
Σ E_L Volts vs NHE
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
−2
−1
0
1
2
3
4